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## The Reaction of *p*-Toluenesulfonamide with Several Compounds Capable of Forming Intermediate Cation

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First, the Ritter reaction using *p*-toluenesulfonamide instead of nitriles has been accomplished under the well known Ritter's conditions. Secondary, the reaction of *p*-toluenesulfonamide with chloronium ions derived from cycloalkenes and *t*-butyl hypochlorite has been found to occur. But, the occurrence of reaction has been recognized only in such circumstances that the desired reaction compete with *N*-chlorination of *p*-toluenesulfonamide by *t*-butyl hypochlorite. Thirdly, it has been found that, under the catalytic action of  $\text{ZnCl}_2$ , *p*-toluenesulfonamide is able to react with an aminomethyl ether and with aminomethyl sulfides affording *N*-alkoxymethyl- and *N*-alkylthiomethyl-*p*-toluenesulfonamides, respectively. These three kinds of reactions will demonstrate that *p*-toluenesulfonamide is capable of trapping the cationic intermediates.

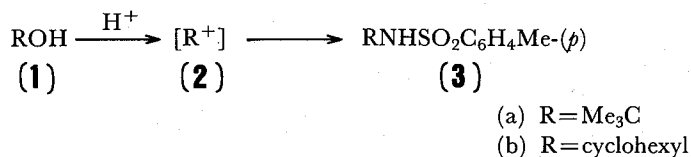
**KEY WORDS:** Ritter reaction/ *p*-Toluenesulfonamide/ Cycloalkenes/ *t*-Butyl hypochlorite/ *N*-Alkoxymethyl-*p*-toluenesulfonamide/ *N*-Alkylthiomethyl-*p*-toluenesulfonamide/

The nitrile source in the Ritter reaction has seen extensive investigation. Not only aliphatic and aromatic nitriles, but also those having  $\text{C}=\text{C}$  bond, halo, hydroxy, alkoxy, amino, or alkoxycarbonyl have been used. Other compounds such as hydrocyanic acid, cyanogen, cyanogen chloride, cyanamide, *l*-cyanoformamide, and dicyandiamide have also been successfully employed.<sup>1)</sup> However, no report has been found in the literature concerning the employment of *p*-toluenesulfonamide instead of the nitriles in the Ritter reaction. Recently, the reactions of olefins with *p*-toluenesulfonamide in the presence of phenylselenenyl chloride has been reported.<sup>2)</sup> This gave us a suggestion that an interaction between *p*-toluenesulfonamide and the so-called "Ritter intermediate" is possible to occur. Thus, the Ritter reaction in which *p*-toluenesulfonamide is used instead of the nitriles was successfully carried out by using 95% sulfuric acid with or without glacial acetic acid as a diluent. This successful result prompted us to investigate consequently the following reactions. We have investigated the reaction between *p*-toluenesulfonamide and the chloronium ion which are easily derived by the reaction of *t*-butyl hypochlorite with some cycloalkenes. Further, the reaction of *p*-toluenesulfonamide with the cations derived by coordinating  $\text{ZnCl}_2$  to an aminomethyl ether or aminomethyl sulfides providing *N*-alkoxymethyl- or *N*-alkylthiomethyl-*p*-toluenesulfonamides have been studied. The accomplishment of these three kinds of reactions using *p*-toluenesulfonamide will demonstrate that *p*-toluenesulfonamide is capable of trapping the cationic intermediates under the appropriate reaction conditions.

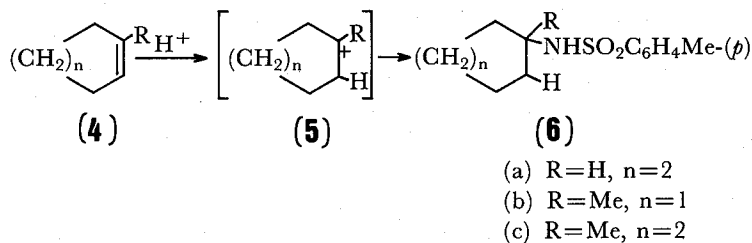
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## RESULTS AND DISCUSSION

The Ritter reaction was carried out in 95% sulfuric acid with or without glacial acetic acid as a diluent at room temperature. The procedure is classified as Procedure A or B (see experimental part). The results obtained by using *t*-butyl alcohol, cyclohexanol, cyclohexene, 1-methyl-1-cyclopentene, and 1-methyl-1-cyclohexene as the carbonium ion source are summarized in Table I.



Scheme 1.



Scheme 2.

Table II. Three Components Reaction of *p*-Toluenesulfonamide, Cycloalkene,

Run	Cycloalkene (equiv.)	Equiv. of <i>t</i> -butyl hypochlorite	Procedure <sup>a)</sup>	Reaction period(h) <sup>b)</sup>
1	Cyclohexene (2)	2	A	20
2	Cyclohexene (2)	2	B	20
3	Cyclohexene (2)	2	C	20
4	Cyclohexene (2)	1	D	42
5	Cyclohexene (2)	2	E	20 <sup>d)</sup>
6	Cyclopentene (2)	2	A	20
7	Cyclopentene (2)	2	B	20
8	Cyclopentene (2)	2	C	20
9	Cyclopentene (1)	1	D	42
10	Cycloheptene (2)	2	A	20
11	Cycloheptene (2)	2	B	20
12	Cycloheptene (2)	2	C	20
13	Cycloheptene (1)	1	D	42

<sup>a)</sup> See experimental part.

<sup>b)</sup> Reaction period after the addition of a cycloalkene into the reaction system.

<sup>c)</sup> Isolated yield by column chromatography based on *p*-toluenesulfonamide.

<sup>d)</sup> Reaction period after the addition of *p*-toluenesulfonamide into the reaction system.

Reaction of *p*-Toluenesulfonamide with Several Cations.

Table I. The Ritter Reaction between *p*-Toluenesulfonamide and Alcohols and Cycloalkenes

Run	Alcohol or cycloalkene	Procedure <sup>a)</sup>	Reaction period(h) <sup>b)</sup>	Product	Yield <sup>c)</sup> (%)
1	<i>n</i> -Butyl alcohol	B	18	<b>3a</b>	59
2	Cyclohexanol	A	24	<b>3b</b> <sup>d)</sup>	41
3	Cyclohexene	A	24	<b>6a</b> <sup>d)</sup>	44
4	1-Methyl-1-cyclopentene	B	18	<b>6b</b>	51
5	1-Methyl-1-cyclohexene	B	18	<b>6c</b>	53

a) See experimental part.

b) Reaction period at room temperature.

c) Isolated yield by column chromatography based on *p*-toluenesulfonamide.

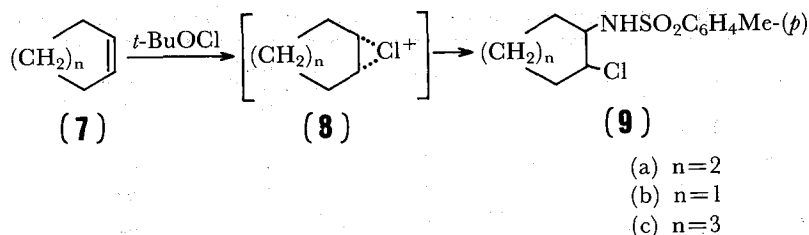
d) The product (**3b**) is identical to **6a**.

Next, the reaction of *p*-toluenesulfonamide with cycloalkene in the presence of *t*-butyl hypochlorite in 1, 2-dichloroethane were carried out under different reaction conditions. The procedure is classified as Procedure A, B, C, D, and E depending upon whether the molar ratio of three reagents is 1:2:2 or 1:1:1 and further upon whether the three reagents were mixed in 1, 2-dichloroethane from beginning or not (see experimental part). The results are summarized in Table II.

Two preliminary experiments concerning *N*-chlorination of *p*-toluenesulfonamide by *t*-butyl hypochlorite were carried out. According to Procedure B or C, *p*-toluenesulfonamide (1.71 g, 10 mmol) and *t*-butyl hypochlorite (2.26 ml, 20 mmol) in 1, 2-dichloroethane (30 ml) were mixed below room temperature, and the mixture was stirred

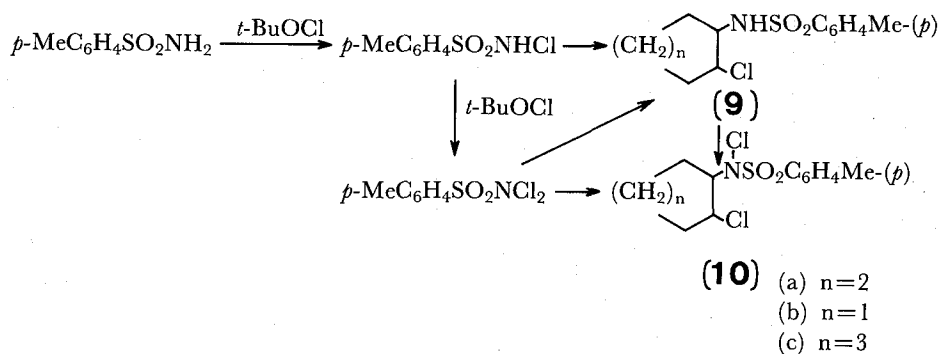
and *t*-Butyl Hypochlorite in 1, 2-Dichloroethane

Yield(%) <sup>c</sup> of		Sum of the yields (%)	Recovered <i>p</i> -toluene- sulfonamide (%)
9	10		
82	11	93	<2-3
25	35	60	26
24	35	59	
28	6	34	
65	6	71	
21	77	98	0
28	38	66	
23	43	66	
19	31	50	
22	75	97	0
11	62	73	
7	64	71	24
23	24	47	



Scheme 3.

at room temperature during 3 h. Then, all volatile substances were removed under reduced pressure to afford a solid mixture. It has been found to consist of 69% of *N*, *N*-dichloro-*p*-toluenesulfonamide, 6% of *N*-chloro-*p*-toluenesulfonamide, and 25% of *p*-toluenesulfonamide by  $^1\text{H}$  NMR spectroscopy. On the other hand, a solid mixture obtained similarly from *p*-toluenesulfonamide and 1 equiv. of *t*-butyl hypochlorite has been found similarly to consist of 21, 29, and 50% in the order above-mentioned. These two results indicate that *N*-chlorination of *N*-chloro-*p*-toluenesulfonamide occur more rapidly than that of *p*-toluenesulfonamide itself and that the deficiency of *t*-butyl hypochlorite, if it occur, act most directly in such a way that the latter *N*-chlorination doesn't occur. Thus, the presence of 25% of *p*-toluenesulfonamide in the above solid mixture seems to be correct, and it was recovered unaltered in spite of further treatment (see runs 2 and 12 in Table II). As can be seen from Table II, the results in runs 2 and 3 are almost same, suggesting that, in run 2, the main part of applied *t*-butyl hypochlorite was consumed by *p*-toluenesulfonamide within 3 h, and afterwards the presence of residual *t*-butyl hypochlorite in the reaction system may be negligible. Such the presumption may be applicable more precisely in run 1, because the charged *t*-butyl hypochlorite is consumed by both *p*-toluenesulfonamide and cyclohexene. Judging from the results in Table II, the same interpretation will be permitted also when cyclopentene or cycloheptene was used instead of cyclohexene. Thus, the reactions occurred in the runs conducted by Procedure B or C are as those as outlined in Scheme 4. As to the reaction steps depicted in Scheme 4, the conversion of **9** into **10** by *N*, *N*-dichloro-*p*-toluenesulfonamide (not by *t*-butyl hypochlorite

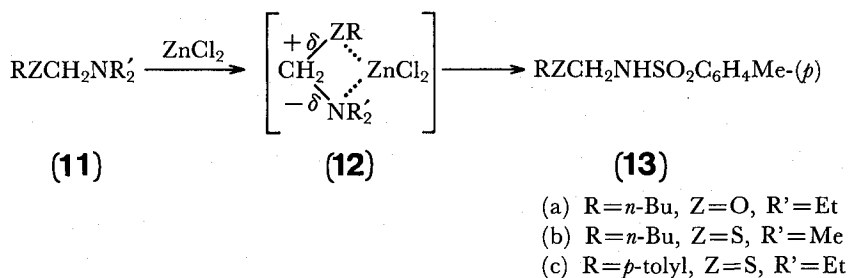


Scheme 4.

as above-mentioned) has been recognized separately in the case in which the cycloalkene component of **9** is cyclohexene. Thus, the stirring of **9a** with *N*, *N*-dichloro-*p*-toluenesulfonamide in 1, 2-dichloroethane at room temperature easily afforded **10a**. Also, the occurrence of reactions between *N*, *N*-dichloro-*p*-toluenesulfonamide and cycloalkenes affording **9** have been already ascertained in the analogous cases.<sup>3)</sup> If the reaction doesn't occur, the yield of **9** in the runs conducted by Procedure B or C will never exceed 6%. The molar quantity of consumed *p*-toluenesulfonamide according to Scheme 4 is equal to the sum of values for both product, **9** and **10**. This hypothesis seems to be reliable or, at least, such that as leads to minor error in consideration of the calculable material balance concerning the results in Table II as well as of that all the reactions depicted in Scheme 4 are as those as proceed stoichiometrically. This may be also applicable for the reactions depicted in Scheme 3. Thus, 60 or 59% of the employed *p*-toluenesulfonamide was consumed in run 2 or 3. In run 1, however, 93% of the amide was consumed; the difference, 33 or 34%, will give an indication of the occurrence of the reaction depicted in Scheme 3. When cyclopentene and cycloheptene were used instead of cyclohexene (in runs 6 and 10), 32 and 24–26% were obtained, respectively, as such the difference. However, these values are brought about by minimum evaluation, because the reactions depicted in Scheme 4 will be depressed in the runs conducted by Procedure A due to the concurrent occurrence<sup>4)</sup> of the reactions depicted in Scheme 3. Probably, in runs 1, 6, and 10 the both processes essentially compete each other. Thus, it becomes clear that *p*-toluenesulfonamide is able to trap the intermediate chloronium ions (**8**). In run 5 conducted by Procedure E, in which the formation of chloronium ion (**8a**) was allowed to precede, 65% yield of **9a** was obtained. Although **8a** might formed by a reversible process, this value seems to be near to the upper limit of the yield of **9a** when the desired reaction alone occurred. The result in run 1 can be easily understood in comparison with that in run 2 or 3. The yield of **10a** is diminished due to the decreased yield of intermediate *N*, *N*-dichloro-*p*-toluenesulfonamide. On the other hand, the competitive occurrence of the desired reaction to a large extent results in the higher yield of **9a**. As can be seen from the result in run 11 or 12, it is clear that, in these runs, such reactions as those provide **10c** prevail. In run 10, these reactions must be somewhat depressed, but the desired reaction will make up for the decrease in yield of **10c**. However, it is difficult to understand why the yield of **10b** in run 6 increased greatly compared with that in run 7 or 8. But the result in run 2 or 3 and that in run 7 or 8 possess a same tendency such as two products, **9** and **10**, are produced in roughly equal amounts. Nevertheless, the monochloro derivative (**9a**) was the main product in run 1 using cyclohexene, on the other hand, the dichloro derivative (**10b**) was produced mainly in run 6 with cyclopentene. Only this experimental fact was unexpected and incomprehensible for us.

Lastly, *p*-toluenesulfonamide was allowed to react with an aminomethyl alkyl ether and with aminomethyl alkyl sulfides in the presence of  $\text{ZnCl}_2$ . The results are summarized in Table III.

As can be seen from Scheme 5, these reactions seem to proceed *via* the intermediate (**12**). The attack of *p*-toluenesulfonamide to **12** will bring about the bond cleavage between the central C and N in **12**. It is well known<sup>5,6)</sup> that, in the reaction of nucleophilic reagents with aminomethyl ethers and with aminomethyl sulfides such as **11a**,



Scheme 5.

Table III. The Reaction of *p*-Toluenesulfonamide with an Aminomethyl Ether and with Aminomethyl Sulfides in the Presence of ZnCl<sub>2</sub>

Run	Aminomethyl ether or aminomethyl sulfide	Reaction period(h) <sup>a)</sup>	Product	Yield(%) <sup>b)</sup>
1	<i>N</i> , <i>N</i> -Diethylaminomethyl <i>n</i> -butyl ether	20	<b>13a</b>	48
2	<i>N</i> , <i>N</i> -Dimethylaminomethyl <i>n</i> -butyl sulfide	24	<b>13b</b>	67
3	<i>N</i> , <i>N</i> -Diethylaminomethyl <i>p</i> -tolyl sulfide	24	<b>13c</b>	87

<sup>a)</sup> Reaction period at room temperature.<sup>b)</sup> Isolated yield by column chromatography based upon *p*-toluenesulfonamide.

**11b**, and **11c**, the reaction proceeds in such a way that the alkoxy and alkylthio groups of the latter compounds are replaced, respectively. In the present reaction, however, the amino group of **11a**, **11b**, and **11c** has been replaced. This may be the first observation concerning the unusual behavior of a aminomethyl ether and aminomethyl sulfides. Although no search has been made to secure an optimum amount of ZnCl<sub>2</sub>-catalyst as well as the best reaction conditions, the present reaction will give an easy route to prepare *N*-alkoxymethyl- and *N*-alkylthiomethyl-*p*-toluenesulfonamides. Also, the compound (**13a**) was easily converted into 1, 3, 5-tris(*p*-tolylsulfonyl)hexahydro-*s*-triazine (**14**) by heating **13a** in ethanol (see experimental part), but the other compounds, **13b** and **13c**, didn't undergo such the alteration.

## EXPERIMENTAL

**The Ritter Reaction between *p*-Toluenesulfonamide and an Alcohol or a Cycloalkene.—Procedure A.** *p*-Toluenesulfonamide (4.28 g, 25 mmol) was mixed with either one of cyclohexanol (2.50 g, 25 mmol) and cyclohexene (2.46 g, 30 mmol). To the mixture was added dropwise sulfuric acid (5 ml, 95%) under cooling. After the addition, the mixture was stirred at room temperature during 24 h, and then poured into 50 ml of water. It was neutralized with aqueous Na<sub>2</sub>CO<sub>3</sub> and extracted with ethyl acetate (25 ml×5). The combined extracts were washed with brine (30 ml), dried over Mg SO<sub>4</sub>, and concentrated under reduced pressure to afford a residue which was purified by column

Reaction of *p*-Toluenesulfonamide with Several Cations.Table IV. Mp and <sup>1</sup>H NMR Spectral Data of the Products (**3**), (**6**), (**9**), (**10**), (**13**), and (**14**)

Product	Mp (°C) (lit., mp)	Recrystallized from	<sup>1</sup> H NMR (δ, in CDCl <sub>3</sub> )
<b>3a</b>	110–112 (112–113) <sup>7)</sup>	Hexane	1.23(s, 9H), 2.44(s, 3H), 5.10(s, 1H), and 7.1–7.9 (m, 4H)
<b>3b</b>	83.5–84.5 (85.7–86.4) <sup>8)</sup>	Hexane	1.0–1.5(m, 6H), 1.5–2.0(m, 4H), 2.43(s, 3H), 3.0–3.3 (m, 1H), 4.78(d, 1H), and 7.1–7.9(m, 4H)
<b>6b</b>	92.5–94.5	Hexane	1.25(s, 3H), 1.3–2.1(m, 8H), 2.41(s, 3H), 5.36(s, 1H), and 7.1–8.0 (m, 4H)
<b>6c</b>	104–106	Hexane	1.17(s, 3H), 1.2–2.2(m, 10H), 2.45(s, 3H), 5.01(s, 1H), and 7.2–8.0(m, 4H)
<b>9a<sup>a)</sup></b>	99–101 (101–102) <sup>9)</sup>	Hexane	1.0–2.4(m, 8H), 2.43(s, 3H), 2.9–3.5(m, 1H), 3.5–4.0 (m, 1H), 5.40(d, 1H), and 7.2–8.0(m, 4H)
<b>9b</b>	87–88.5	Hexane	1.2–2.4(m, 6H), 2.44(s, 3H), 3.4–3.8(m, 1H), 3.9–4.3 (m, 1H), 5.69(d, 1H), and 7.2–7.9(m, 4H)
<b>9c</b>	84–86	Hexane	1.1–2.4(m, 10H), 2.43(s, 3H), 3.3–3.7(m, 1H), 3.8– 4.2(m, 1H), 5.63(d, 1H), and 7.2–8.0(m, 4H)
<b>10a<sup>a)</sup></b>	70 <sup>b)</sup>	Hexane	1.2–2.5(m, 8H), 2.45(s, 3H), 3.5–4.5(m, 2H), and 7.2– 8.0(m, 4H)
<b>10b</b>	50 <sup>b)</sup>	Petroleum ether	1.5–2.3(m, 6H), 2.45(s, 3H), 3.9–4.3(m, 1H), 4.5–4.9 (m, 1H), and 7.2–8.0(m, 4H)
<b>10c</b>	55–60 <sup>b)</sup>	Petroleum ether	1.2–2.4(m, 10H), 2.46(s, 3H), 4.0–4.7(m, 2H), and 7.2– 8.0(m, 4H)
<b>13a</b>	45	Benzene/Petroleum <sup>c)</sup> ether	0.6–1.1(m, 3H), 1.0–1.6(m, 4H), 2.40(s, 3H), 3.24 (t, 2H), 4.60(d, 2H), 5.9–6.5(m, 1H), and 7.1–7.9 (m, 4H)
<b>13b</b>	59–61.5	Hexane	0.7–1.0(m, 3H), 1.2–1.7(m, 4H), 2.42(s, 3H), 2.53 (t, 2H), 4.04(d, 2H), 4.6–4.9(m, 1H), and 7.2–7.9 (m, 4H)
<b>13c</b>	94–95	Hexane + Ethyl acetate <sup>d)</sup>	2.31(s, 3H), 2.43(s, 3H), 4.41(d, 2H), 4.7–5.0(m, 1H), and 7.0–7.8(m, 8H)
<b>14</b>	164–165.5 (168–169) <sup>10)</sup>	Ethanol	2.42(s, 9H), 4.57(s, 6H), and 7.2–7.8(m, 12H)

<sup>a)</sup> The compound (**9a**) is *trans*-isomer, and **10a** is also *trans*-isomer because it could be derived from **9a**. The other compounds (**9b**), (**9c**), (**10b**), and (**10c**) will be *trans*-isomers, but this is uncertain.

<sup>b)</sup> Determined by heating the crystal in a capillary tube very quickly, because the crystal decomposes under heating. Thus, only a rough value was obtained.

<sup>c)</sup> Reprecipitated with benzene and petroleum ether, because heating **13a** in most solvents bring about the decomposition and successive trimerization into **14**.

<sup>d)</sup> Hexane containing a small amount of ethyl acetate.

chromatography on silica gel using 50% ethyl acetate-hexane as a eluent.

**Procedure B.** To a stirred, cooled mixture of glacial acetic acid (20 ml) and sulfuric acid (2 ml, 95%) was added *p*-toluenesulfonamide (0.86 g, 5 mmol). After making sure that the cooled mixture becomes homogeneous, either one of *t*-butyl alcohol (0.74 g, 10 mmol), 1-methyl-1-cyclopentene (0.82 g, 10 mmol), and 1-methyl-1-cyclohexene (0.96 g, 10 mmol) was added under stirring. The mixture was stirred at room temperature during 18 h, and then poured into 100 ml of water. It was extracted with ethyl acetate (30 ml×3). The combined extracts were washed repeatedly with 10% aqueous ammonia, dried over MgSO<sub>4</sub> and evaporated under reduced pressure to afford a residue which



was purified as above.

**Three Components Reaction of *p*-Toluenesulfonamide, a Cycloalkene, and *t*-Butyl Hypochlorite.—Procedure A.** In 1, 2-dichloroethane (30 ml) *p*-toluenesulfonamide (1.71 g, 10 mmol), a cycloalkene (20 mmol), and *t*-butyl hypochlorite (2.26 ml, 20 mmol) were mixed below room temperature. The mixture was stirred at room temperature during appropriate time, and then poured into 200 ml of water. The organic layer was separated and the aqueous layer was extracted with 1, 2-dichloroethane (30 ml×3). The combined organic layer was dried over Mg SO<sub>4</sub> and most of the solvent was evaporated. The residue was subjected to column chromatography on silica gel using 30% ethyl acetate-hexane as a eluent.

**Procedure B.** In 1, 2-dichloroethane (30 ml) *p*-toluenesulfonamide (1.71 g, 10 mmol) and *t*-butyl hypochlorite (2.26 ml, 20 mmol) were mixed below room temperature. The mixture was stirred at room temperature during 3 h, and then a cycloalkene (20 mmol) was added below room temperature. The mixture was again stirred at room temperature during appropriate time, and worked up as above.

**Procedure C.** This procedure was the same as Procedure B except that, after the stirring during 3 h above-mentioned, all volatile substances were removed under reduced pressure and 30 ml of 1, 2-dichloroethane and a cycloalkene (20 mmol) were added subsequently below room temperature. Then, the mixture was allowed to react and worked up as above.

**Procedure D.** The reaction was carried out with *p*-toluenesulfonamide (1.71 g, 10 mmol), a cycloalkene (10 mmol), and *t*-butyl hypochlorite (1.13 ml, 10 mmol) in 1, 2-dichloroethane (30 ml) in the same manner as Procedure A, but the reaction period was 42 h.

**Procedure E.** This procedure refers to only the case using cyclohexene as the cycloalkene component. In 1, 2-dichloroethane (30 ml) cyclohexene (1.64 g, 20 mmol) and *t*-butyl hypochlorite (2.26 ml, 20 mmol) were mixed below room temperature. The mixture was stirred at room temperature during 5 h, and then *p*-toluenesulfonamide (1.71 g, 10 mmol) was added below room temperature. The mixture was further stirred at room temperature during 20 h, and worked up as above.

**Reaction of *p*-Toluenesulfonamide with an Aminomethyl Ether and with Aminomethyl Sulfides in the Presence of ZnCl<sub>2</sub>.**—To a stirred solution of *p*-toluenesulfonamide (1.71 g, 10 mmol) and either one of **11a** (1.91 g, 12 mmol), **11b** (1.77 g, 12 mmol), and **11c** (2.52 g, 12 mmol) in 1, 2-dichloroethane (30 ml) was added ZnCl<sub>2</sub> (1.64 g, 12 mmol). The mixture was stirred at room temperature during appropriate time and poured into 50 ml of water. The organic layer was separated and the aqueous layer was extracted with dichloromethane (30 ml×2). The combined organic layers were washed with 30 ml of water, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure affording a residue which was subjected to column chromatography on silica gel using 50% ethyl acetate-hexane as a eluent.

**Conversion of *N*-Butoxymethyl-*p*-toluenesulfonamide (**13a**) into 1, 3, 5-Tris-(*p*-tolylsulfonyl)hexahydro-*s*-triazine (**14**).**—A solution of **13a** (0.23 g, 0.89 mmol) in ethanol (6 ml) was refluxed during 6 h. The solution was evaporated under reduced pressure to afford a residue which was subjected to column chromatography on silica gel using 50%

ethyl acetate-hexane as a eluent. The yield of **14** was 87%.

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